XANES IN FAST ION CONDUCTING GLASSES AgI: Ag2O: B2O3

G. Dalba, P. Fornasini, F. Rocca, E. Burattini

To cite this version:
G. Dalba, P. Fornasini, F. Rocca, E. Burattini. XANES IN FAST ION CONDUCTING GLASSES AgI: Ag2O: B2O3. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-749-C8-752. <10.1051/jphyscol:19868142>. <jpa-00226043>

HAL Id: jpa-00226043
https://hal.archives-ouvertes.fr/jpa-00226043
Submitted on 1 Jan 1986
XANES IN FAST ION CONDUCTING GLASSES AgI:Ag₂O:B₂O₃

G. DALBA*,**, P. FORNASINI*,***, F. ROCCA** and E. BURATTINI**

*Dipartimento di Fisica e Unità CISM, Università di Trento, I-38050 Povo (Trento), Italy
**Centro di Fisica degli Stati Aggregati e Impianto Ionico del CNR, I-38050 Povo (Trento), Italy
***INFN, Laboratori Nazionali di Frascati, P.O. Box 13, I-00044 Frascati, Italy

Abstract - The XANES at the Ag L edges of glasses Ag₂O:B₂O₃, analyzed in terms of electronic transitions to unoccupied molecular orbitals, confirm previous EXAFS results and support a model for the bond between Ag and the borate network. When AgI is added, the XANES allow to determine the fraction of Ag ions bonded to the borate network.

INTRODUCTION

The glasses AgI:Ag₂O:B₂O₃ are typical examples of "fast ion conducting" glasses: their d.c. ionic conductivity covers a range of several orders of magnitude as a function of composition /1/. This property is interesting for their possible utilization in electrochemical devices. The mechanism of ionic conduction is not yet fully understood: in particular it is controversial whether all Ag⁺ ions are equivalent or the Ag⁺ ions bonded to iodine play a predominant role /2,3/. A thorough structural knowledge would greatly contribute to the solution of this problem.

The structure of the boron-oxygen network in the binary matrix Ag₂O:B₂O₃ has been quite well established by NMR, Raman and IR measurements. The coordination of boron is progressively changed from planar triangular (BO₃) to tetrahedral (BO₄) by addition of Ag₂O so long as the molar ratio n=BO₃/Ag₂O > 2. For n>2 the boron-oxygen network is fully connected, i.e. each oxygen atom is bonded to two boron atoms /1/.

The local arrangement of the mobile cation Ag⁺ is little known. Ag⁺ is supposed to be bonded to the negatively charged BO₄ tetrahedra but the nature of the bond has to be clarified.

Due to its selectivity, XAS is particularly suited to study the short range coordination of the modifier cation (in this case silver) in oxide glasses /4/. The Ag-O coordination in the binary matrix Ag₂O:B₂O₃ (n=2,3,4,6) has been recently studied by EXAFS /5/. The main results are summarized in Fig.1. The interatomic distance Ag-O, which is r=2.044 Å in the crystalline model compound Ag₂O, varies from r=2.23+0.05 Å to 2.34+0.05 Å in the glasses, slightly decreasing when the Ag₂O content increases.
The open circle represents the model compound Ag$_2$O. For the glass $n=2$ the best fit to the experimental EXAFS requires a further Ag-O coordination at $r=1.39$ Å, consistent with the presence of non-bridging oxygens in the borate network for high Ag$_2$O contents.

The coordination numbers are dispersed around the value $N=2$. The behaviour of their distribution as a function of $n$ is strongly correlated to that of the disorder parameters $\Delta q^2$, due to the shortness of the $k$ range of the EXAFS signal. The EXAFS results are consistent with the hypothesis that silver in the glasses is coordinated to two oxygens, with disorder parameters not sensibly higher than that of crystalline Ag$_2$O.

To test the validity of this structural hypothesis, in this work we analyze the fine structures at the edges Ag $L_1$ and Ag $L_3$ in crystalline Ag$_2$O and in the binary glass matrix Ag$_2$O:B$_2$O$_3$ in terms of transitions to unoccupied molecular orbitals. The analysis is then extended to the ternary glasses AgI:Ag$_2$O:B$_2$O$_3$ to study the effects of the addition of AgI on the bond Ag-O.

**RESULTS AND DISCUSSION. I. BINARY MATRIX**

At the edge Ag $L_1$ the spectra of the glasses are remarkably different from those of Ag and of Ag$_2$O (Fig. 2a). At the edge Ag $L_3$ the spectra of the glasses and of Ag$_2$O are very similar within the first 10 eV, characterized by a peak at about 1 eV and a shoulder at about 6 eV (Fig. 2b).

The crystalline structure of Ag$_2$O, like that of Cu$_2$O, is characterized by a linear O-Ag-O coordination of silver with two oxygens. Hulbert et al. /6/ attribute the white peak at the edge Cu $L_3$ in Cu$_2$O to electronic transitions to an s-like antibonding molecular orbital. In view of the close similarity of electronic properties and crystal structure of Ag$_2$O and Cu$_2$O, this attribution of the peak can be reasonably extended to Ag$_2$O.

The EXAFS results (Fig. 1) and the XANES can be explained by the following model. Silver ions are not randomly dispersed in the interstices of the glass. They are instead linked to the borate network by a chemical bond with two oxygens like in Ag$_2$O. Since all oxygens are bridging between the structural units B$_2$O$_3$ and B$_2$O$_4$, the most reasonable bond is between Ag and two oxygens belonging to the same edge of a B$_2$O$_4$ tetrahedron. The O-Ag-O chain cannot thus be linear as in Ag$_2$O. The distortion of the O-Ag-O chain should affect by far more the directional p orbitals than the isotropic s orbitals: this can explain similarities (edge $L_3$) and differences (edge $L_1$) between the glasses.
XANES of glasses and Ag$_2$O. The Ag-O distances obtained by EXAFS are consistent with an 0-Ag-0 angle of about 64 degrees. The quite strong Ag-O bond is independent from glass composition (at least for $n>2$). Only the Ag-O distance slightly decreases when increasing the Ag$_2$O content; this probably reflects the strengthening of the structure when the boron coordination progressively changes from planar triangular to tetrahedral. A local order around the modifier cation has been found also in sodium borate glasses by EXAFS and XRD /7,8/ and in sodium phosphate glasses by neutron diffraction /9/. The coordination number is however lower (N=2) for Ag in borate glasses and for Na in phosphate glasses than for Na in borate glasses (N=5-6).

Fig.2 - Fine structures of Ag, Ag$_2$O and binary glasses Ag$_2$O n B2O3 at the edges Ag L$_1$ (a) and Ag L$_3$ (b). Fine structures of ternary glasses (AgI)$_x$(Ag$_2$OnBz0$_3$)$_{1-x}$ and $\beta$-AgI at the edge Ag L$_3$ (c). The zero of the energy scale has been chosen at the maximum of the first derivative. The heigths of the spectra have been normalized in the region 15-20 eV.

RESULTS AND DISCUSSION. II. TERNARY GLASSES

In Fig.2c the fine structures at the edge Ag L$_3$ for ternary glasses (AgI)$_x$(Ag$_2$OnBz0$_3$)$_{1-x}$ with $n=4$ and $x$ varying from 0.1 to 0.55 are compared with those of the corresponding binary matrix ($n=4$, $x=0$) and of crystalline $\beta$-AgI ($x=1$). The peak at 1 eV is present in the spectra of all the glasses, its intensity decreasing when increasing the AgI content.

On the grounds of the preceding discussion we consider the white peak a fingerprint of an 0-Ag-0 distorted bond of silver with the borate network. This quite strong bond of Ag with the borate network is thus not modified by the insertion of AgI into the glass.

In ternary glasses a fraction $X=\text{EIJ}/\text{EAgI}=x/(2-x)$ of silver ions comes from the component AgI, a fraction 1-$X$ from Ag$_2$O. The intensity of the peak at 1 eV in Fig.2c monitors the fraction of silver ions actually coordinated to the borate network.
To evaluate the fraction of Ag+ ions bonded to the borate network as a function of \( x \), the spectra of the ternary glasses in Fig.2c have been compared with a weighted linear superposition of the spectra of the binary matrix and of \( \beta \)-AgI. This is an approximate procedure, since the bond Ag-I is probably different in the glasses with respect to \( \beta \)-AgI; on the other hand the spectrum of \( \beta \)-AgI is quite smooth, so we suppose that the contribution of the Ag-I bond cannot be very different in the glasses (say in a more disordered situation).

The linear superpositions which best fit the experimental spectra in the energy region of the peak (-5 to 5 eV) are shown in Fig.3. The agreement between theory and experiment is very good for the glass \( x=0.3 \). The values of the fitting coefficients (0.19 and 0.81) are very close to the stoichiometric ones (\( X=0.18, \ 1-X=0.82 \)). For the other glasses the fitting coefficients slightly underestimate \( 1-X \) and overestimate \( X \) (10% for the glass \( x=0.1 \), 20% for the glass \( x=0.55 \)).

These data indicate that when adding AgI to the glass the fraction of Ag+ ions bonded to the borate network is almost unchanged. The slight discrepancies between fitting coefficients and stoichiometric values can depend on experimental uncertainties and/or on the inadequacy of the edge structures of \( \beta \)-AgI to describe the Ag-I bond in the glasses. They can also depend on the contribution of mixed bonds I-Ag\<\text{Z0} to the experimental spectra.

Fig. 3 - Experimental spectra of ternary glasses (continuous lines) compared with linear superpositions of the spectra of binary glass (\( x=0 \)) and \( \beta \)-AgI (\( x=1 \)) (dots). The fit is optimized in the region of the peak (-5 to 5 eV).

REFERENCES

/2/ H.L.Tuller and M.W.Barsoum, J. Non-crystalline Sol. 73, 331 (1985)
/5/ G.Dalba, P.Fornasini, F.Rocca, E.Bernieri, E.Burattini and S.Mobillo, J. Non-crystalline Sol., to be published